

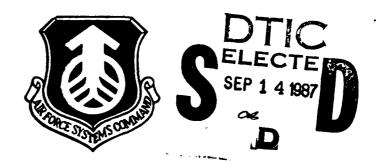
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HIGH-MOLECULAR COMPOUNDS (Selected Articles)



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HUMAN TRANSLATION

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TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WPAFB, OHIO.

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Date 24 August

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Пп	Пп	P, p	Яя	Як	Ya, ya

*ye initially, after vowels, and after b, b; e elsewhere. When written as & in Russian, transliterate as ye or &.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh l
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian	English		
rot	curl		
1g	log		

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METHACRYLIC POLYMERS WITH A SYNDIOTACTIC STRUCTURE ON A BASE OF ESTERS OF PHOSPHOROUS-CONTAINING ALCOHOLS

L.D. Budovskaya, Ye.N. Rostovskiy,

A.V. Sidorovich, Ye.V. Kuvshinskiy

Submitted 26 Dec 1966

Dear Editor,

It was reported in [1] that by means of radical polymerization polymers of methacrylic esters of phosphorous-containing alcohols (PFME) of the following series were obtained:

CH₃

$$CH_{2}=C-C-OCH_{2}(CF_{2}-CF_{3})_{n}H,$$

$$0$$

where n=2-4.

These polymers themselves were not crystallized and therefore it would be impossible to determine their stereostructure by X-ray diffraction. In connection with this we obtained products which were reliably identified from them by means of polymer-analog conversions. For this purpose one of the esters (polyoctafluoroamyl methacrylate) was converted into polymethacrylic acid by hydrolysis in an alkaline medium. The poly acid was methylated by diazomethane into polymethyl methacrylate (PMMA). It turned out that the PMMA which was formed in this case is crystallized already in the process of being produced, without requiring the swelling in 4-heptanone which is usually used [2, 3]. The Debye crystallograms of PMMA from PFME were sharp and

contained 5 rings for PMMA₂₀, obtained from ester which was polymerized at 20° (drawing), and 3-2 rings for PMMA₇₀ which was polymerized at 70° . The interplanar distances coincided with those known for syndiotactic PMMA_K, obtained by low-temperature catalytic polymerization [2] (table).

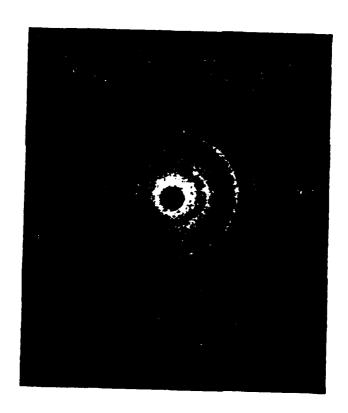
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ПММАю 3 ПММАю [2]	4,46 4,47 4,52	3,86	3,11 3,11 3,08	2,58 2,63	2,21° 2,21°	

Key: (1) Type of PMMA; (2) Interplanar distances, \hat{A} ; (3) according to [2]; (4) * Additional line, not detected in [2].

The glass transition temperatures of the polymers were close (115-120°). Based on these data, PMMA on a base of PFME is a syndiotactic highly-regular polymer. This also proves that the initial perfluoroesters possessed a regular syndiotactic structure. Thus the presence of substituting groups of $(CF_2-CF_2)_nH$ by the polymerizing monomer and the growing polymer radical contributes to the synthesis of regular macromolecules.

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Debye crystallogram of PMMA obtained from polyoctafluoroamylmethacrylate, synthesized by way of the radical mechanism at 20° . Radiation CuK_{oC}, monochromatized by Ni, distance 40 mm.

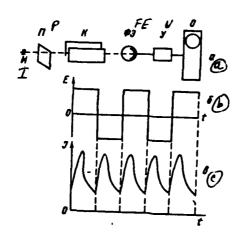
PERMANENT DIPOLE MOMENT IN ASSOCIATIONS OF POLYMETHACRYLIC ACID AND POLYVINYL ALCOHOL

I.F. Yefremov, E.B. D'yakonova, A.A. Spartakov, A.A. Trusov, O.G. Us'yarov

Leningrad Technological Institute im. Lensovet Submitted 25 Apr 66

In a low-concentrated aqueous solution of polymethacrylic acid (PMAK) and polyvinyl alcohol (PVS) mixed associations which have an ordered structure are formed. With a 7% and higher concentration of polymers a gel is precipitated from it, in which the relative content of PMAK and PVS comprises 7:3 with respect to weight or 1:1 with respect to monomer groups [1]. The associations have a globular form, and the gel - a fibrillar structure [2].

The development of anisodiametric aggregates - microfibrils - from the individual associations may be conditioned by the action of the electric forces of the total permanent dipoles. The presence of the latter in a number of high-molecular compounds (proteins, polyesters) is assumed by some investigators, stemming from calculation data [3, ..., and for many colloids in polar media it has been established experimentally [5].



a - Basic layout of the installation: I - light source; P - polaroid; K - cuvette with electrodes, placed in the investigated system; FE - photocell; U - amplifier; O - oscillograph.

b - sign-variable electric square pulses of voltage E;

c - modulation of light which is passing through the investigated system; I - intensity of transmitted light.

For checking this assumption a study was made of the electro-optical properties of aqueous solutions of PMAK (M=84 000) and PVS (alkaline method of saponification, M=87 000). The method is based on the modulation of light which is transmitted perpendicular to the force lines of an electric field through a plane condenser (drawing, a) which is fed by sign-variable electric square pulses of voltage (drawing, b). In our experiments a field with an intensity E=±300 V/cm with a frequency from one to several hertz was used. The modulation of light which is observed (drawing, c) develops as a result of the periodic reorientation of the nonspherical particles in this field, which proves the existence in them of a permanent electric dipole moment [6].

For a 1% solution of PMAK and PVS, in which the association is expressed quite strongly, the modulation of light is not detected. However, this negative result, in view of the spherical form of the associations, still does not indicate the absence of a rigid dipole moment in them. In the same manner there was no modulation of light for individually taken 7% solutions of PMAK and PVS. If the freshly obtained gel, which developed with the mixing of 7% solutions of PMAK and PVS (weight ratio 7:3), is destroyed by vigorous shaking, then a "suspension" of gel pieces is formed. As a result of their irregular form and when a dipole structure is present, the gel pieces should condition a change in the intensity of transmitted light. Actually for such a suspension the modulation of transmitted light was observed quite distinctly when square electric pulses were superimposed. This testifies uniquely to the existence of a rigid electric dipole moment in particles of an aqueous gel of PMAK and PVS.

The formation of a rigid dipole structure is possible as a result both of the unipolar orientation of the hydroxyl and carboxyl groups of the polymers, and of the similar orientation of the dipoles of the water entering into the structure of the associations. An ordered association of polymers, leading to gelatinization if their concentration is sufficient, should correspond to such an orientation. It is possible that the dipole interaction is a significant factor, determining the processes of fiber formation in different systems.

Conclusions

- 1. Studies were made of the electro-optical properties of a macroheterogeneous system, forming in the case of mixing of aqueous solutions of polymethacrylate acid and polyvinyl alcohol.
- 2. Modulation of the transmitted polarized light was detected, which testifies to the existence of a rigid electric dipole moment in the particles of this system.

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INVESTIGATION OF THE KINETICS OF POLYMERIZATION OF COMPOUNDS WHEN AN ACID CHLORIDE OF CARBOXYLIC ACID-TERTIARY AMINE SYSTEM IS PRESENT

S.D. Stavrova, I.P. Chikhacheva, S.S. Medvedev

Moscow Institute of Fine Chemical Engineering im. M.V. Lomonosov Submitted 27 Apr 66

It was demonstrated earlier [1] that systems consisting of tertiary amines and carboxylic acids or their derivatives (esters) can be used as initiators of polymerization of vinyl compounds. Such initiating systems become particularly effective in the case of polymerization of polar media, for example, in aqueous emulsions (1, 2). An analogous initiating system can be presented in the form of the system tertiary amine - acid chloride of carboxylic acid. This system is interesting not only as a new initiator of polymerization, but also because such a system is a certain model for analyzing the primary processes in the reaction of polycondensation.

At the present time the problem concerning the structure of the intermediate complex in the reaction of polycondensation still remains unclear. However, it can be expected that in the reaction process an intermediate complex with a transfer of charge (KPZ) is formed, since tertiary amines are donors, and the acid chlorides - acceptors of electrons:

Acid chloride + amine = (acid chloride...amine).

In certain cases such KPZ can produce radicals which initiate the polymerization of vinyl compounds. As we have demonstrated, in the case of the interaction of benzoyl chloride with dimethylaniline a KPZ is formed, which under the appropriate conditions dissociates into radicals [3]:

$$C_{0}H_{8}-C + : N-C_{0}H_{5} \rightleftharpoons \begin{pmatrix} CH_{8} & CH_{8} \\ C_{0}H_{5}-C & \cdots & N-C_{0}H_{5} \\ Cl & CH_{3} \end{pmatrix} \rightleftharpoons C_{0}H_{8}CO + Cl^{-} + \cdot N-C_{0}H_{5}.$$

The benzoyl radical which is formed in this scheme is initiating.

The results of this work are a part of investigations which we conducted in the area of studying the interaction of haloid acyls with amines for the purpose of clearing up the bond between the elementary act of the reaction of polycondensatic and the initiation of processes of radical polymerization.

The results presented in this article pertain to the kinetics of polymerization of methyl methacrylate (MMA) in the presence of the system benzoyl chloride (BC)-dimethylaniline (DMA) both in bulk and in solution.

Experimental section

Analytical grade benzoyl chloride was distilled three times in a current of nitrogen with lowered pressure. The fraction which was boiled at $60^{\circ}/5$ mm was withdrawn into tubes with a three-way cock and stored under nitrogen.

Acetonitrile (ACN) was purified by means of a single boiling with P_{205} and distilled three times in a current of nitrogen at atmospheric pressure. The fraction which boiled at 81.5° was withdrawn and stored under nitrogen.

Dimethyl sulfoxide (DMSO) was freed of traces of moisture by azeotropic distillation of water with benzene and then distilled twice in a current of nitrogen at atmospheric pressure; the fraction with a b.p. of 1820 was drawn off and stored under nitrogen.

The purification of the remaining initial substances, the dilatometric method of investigating the kinetics of polymerization, and the determination of the molecular weights of the polymers were described earlier [2].

Results of the tests and a discussion of them

Bulk polymerization. The results of the tests on polymerization of the different vinyl compounds in the presence of BC-DMA (equimolecular concentrations are equal to 0.3 mole/1) at 70° showed that based on the rate of polymerization the monomers are arranged in the series:

Acrylonitrile > methyl methacrylate > styrene.

MMA was selected as the monomer for the further detailed kinetic investigations.

The results of the tests for clearing up the influence of each of the components of the initiating system on the rate of polymerization of MMA at 60 and 70° showed that DMA increases the rate of thermal polymerization of MMA and BC does not change it. Previously [1, 2] we had pointed out the possibility of polymerization of MMA when DMA alone was present. However, in contrast to DMA, the aliphatic (triethylamine) and heterocyclic (pyridine) amines, with other conditions being equal, do not bring about the polymerization of MMA.

When attempting to polymerize MMA in the presence of the system BC-tertiary amine, where triethylamine and pyridine were used as the amine, it also turned out that in both cases polymerization does not take place. Furthermore, when solutions of BC and triethylamine or pyridine were decanted in MMA in a dilatometer a precipitate of stable syl ammonium salts was formed, which serves as an explanation for the absence of polymerization of MMA under these conditions (at 60 and 700).

Subsequently all the tests were conducted in the presence of BC with the participation only of the aromatic amine - DMA.

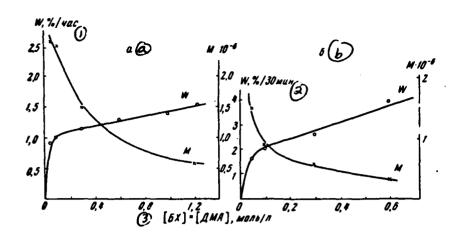


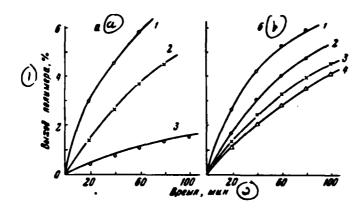
Figure 1. Dependence of the rate of polymerization of MMA at 70° (W) and molecular weights of the polymers (M) on the concentration of equimolecular amounts of BC and DMA:
a - bulk polymerization; b - in ACN.
Key: (1) h; (2) min; (3) [BC]=[DMA], mole/1.

Polymerization of MMA in the presence of BC-DMA with equimolecular proportions of components of the initiating system. The results of the tests on polymerization of MMA in a wide range of equimolecular concentrations of BC and DMA (Fig. 1,a) show that the rate of the reaction increases with an increase in the concentration of the initiator, and the molecular weights of the polymers which are formed are lowered.

MMA (concentrations of BC and DMA equal to 0.3 mole/1) was polymerized at 70, 60 and 50°. On the basis of the results of these tests the overall energy of activation of polymerization of MMA, initiated by the system BC-DMA, was calculated. It was equal to 13.5 kcal/mole.

system. For clearing up the nature of initiation of polymerization with BC-DMA present tests were set up for the copolymerization of MMA with styrene with equimolecular proportions of them in the mixture. The copolymerization was carried out in ampoules at 60° free of oxygen from the air. In a comparison of the content of carbon and hydrogen in the copolymer which was obtained with the data in the literature [4] it turned out that a radical mechanism of initiation takes place, just as in the case of the system benzoic acid (ester of carboxylic acid_-DMA [1].

Polymerization of MMA in solutions. The results of the tests on the polymerization of MMA with the initiating system BC-DMA in solutions showed that the nature of the solvent has a significant influence on the rate of polymerization of MMA. It is evident from the data in Figure 2, a that the rate of the reaction increases with an increase of the dielectric constant of the solvent: DMSO>ACN>MMA.



Subsequently for studying the kinetics of polymerization of MMA in solutions ACN was selected as the solvent. In all the tests the concentration of monomer was equal to 4.68 mole/1.

For the purpose of determining the overall activation energy of polymerization of MMA, initiated by BC-DMA in a solution in ACN, the tests were conducted at 40, 50, 60 and 70°. The concentrations of BC and DMA were equimolecular and equal to 0.3 mole/1. On the basis of the results of these tests the activation energy was calculated. It turned out to be equal to 7.0 kcal/mole.

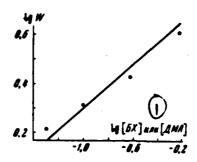


Figure 3. Logarithmic dependence of the rate of polymerization of MMA in ACN at 70° on the concentration of initiator; n=0.45. Key: (1) lg[BC] or [DMA].

Polymerization of MMA in the presence of BC-DMA was carried out at .0° and different equimolecular concentrations of BC and DMA, changing in the range from 0.05 to 0.6 mole/l. The results are given in Fig. 1,b and 2,b, where it can be seen that the rate of polymerization is increased with an increase in the concentration of initiator, and the molecular weights of the polymers which are formed drop. Based on the data in Figure 3 it has been established that the order of the reaction with respect to the initiator is equal to 0.45, which is close to 0.5, i.e., the rate of polymerization of MMA is described by the equation W=k[BC]^{0.5} or W=[DMA]^{0.5}. The same dependence of the rate of the reaction on the concentration of initiator was obtained at 60°; also this dependence is analogous to the equation which was obtained in the case of polymerization of MMA, initiated by the system benzoic acid-DMA [1].

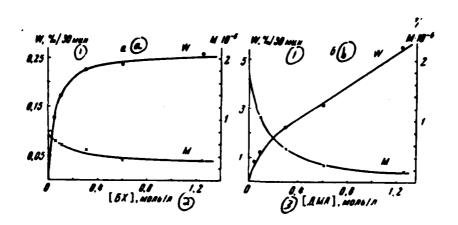


Figure 4. Influence of the concentration of BC (a) and DMA (b) on the rate of polymerization of MM in ACN at 60° (W) and the molecular weights of the polymers (M). Concentrations of DMA (a) and BC (b) are equal to 0.3 mole/l.

Key: (1) min; (2) [BC], mole/l; (3) [DMA], mole/l.

When tests were set up for the polymerization of MMA in the presence of different concentrations of BC, changing in the interval from 0.05 to 1.25 mole/1, and a constant concentration of DMA (0.3 mole/1) it turned out that the rate of the reaction increases with an increase in the amount of BC in the system only up to 0.3 mole/1; with a further increase in the amount of acid chloride the rate of polymerization does not change (Fig. 4,a). As is evident from Figure 4,a, the molecular weights of the polymers are lowered with an increase in the concentration of BC to 0.3 mole/1, then they remain virtually constant. The results of polymerization of MMA in the presence of different concentrations of DMA and a constant concentration of BC, equal to 0.3 mole/1, showed that the rate of the reaction increases, and the molecular weights of the polymers are lowered with an increase in the concentration of amine (Fig. 4,b).

Tests were conducted on the polymerization of MMA in the presence of BC-DMA (equimolecular concentrations equal to 0.3 mole/1) in a solution in ACN, where the concentration of monomer was equal to 0.78, 3.12 and 7.8 mole/1. It turned out that the rate of polymerization of MMA is proportional to the concentration of monomer.

Conclusions

- 1. In an example of the benzoyl chloride (BC)-dimethylaniline (DMA) system it is shown that this system, which can be considered as a model in the primary processes of polycondensation, is the initiator of polymerization of vinyl compounds.
- 2. The kinetics of polymerization of methyl methacrylate (MMA) in the presence of BC-DMA were studied both in bulk and in solution in acetonitrile. It is shown that the effectiveness of initiation increases when polymerization is carried out in polar media.
- 3. Based on the composition of the copolymer MMA with styrene, obtained by the copolymerization of these monomers in the presence of BS-DMA, it was established that the radical mechanism of initiation takes place.
- 4. Values are determined for the overall activation energy of polymerization of MMA in the presence of the BS-DMA system in bulk (13.5 kcal/mole) and in solution in acetonitrile (7.0 kcal/mole).

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